

Quantum dynamics of a hydrogen-like atom in a time-dependent box: Cooling, compressing and diffusive ionization in non-adiabatic regime.

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We study quantum dynamics of one-electron atom confined in a spherical impenetrable box with time-dependent radius. The behavior of the atomic electron interacting with the moving walls of the box is analyzed by computing average binding energy, average force and pressure. Linearly extending, contracting and harmonically breathing boxes are considered in the non-adiabatic regime i.e. when the wall of the box moves with high velocities. It is shown that linearly extending box leads to de-excitation of the atom, while the rapidly contracting box causes the creation of very high pressure on the atom and transition of the atomic electron into the unbound state. In harmonically breathing box diffusive excitation of atomic electron and ionization may occur in analogy with that for atom in a microwave field.

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I. INTRODUCTION

Atoms and molecules confined nanoscale domains have physical properties which are completely different than those of free atoms. Such difference is caused by the modification of boundary conditions imposed for quantum mechanical wave equations (e.g., Schrödinger, Dirac equations) as well as by high pressure induced by the domain boundaries. For free atoms the boundary conditions are imposed in whole space, while for confined atoms one should solve the wave equations with the boundary conditions imposed in finite domain. Due to such modification, properties of the atoms, molecules and matter depend on the shape and size of a confining domain. Spatially confined atoms and molecules appear in many branches of physics, such as ultracold atoms, BEC, atom optic billiards, metallic hydrogen and different topics of nanoscale physics. Moreover, such practically important problems as atom cooling in nanoscale optical traps [1], fabrication of low dimensional nanomaterials [2], manipulation by atoms in optical billiards [3] and creation of a matter under high pressure [4–9] deal with the problem of confined atoms and molecules. A key issue in the study of such systems is the reaction of the electronic structure of an atom on the confining potential [5]. A convenient model for the study of atoms under spatial confinement is the atom-in-box system. Pioneering studies of atom in a box with impenetrable walls date back to the Ref. [9, 10], where effect of the pressure on an atom was explored. Later the problem was studied within the

quantum mechanical approach in different contexts (see, e.g., [9]–[16]).

Experimentally, atom-in-box system can be realized in co-called atom optic billiards which represent a rapidly scanning and tightly focused laser beam creating a time-averaged quasi-static potential for atoms [17]–[21]. By controlling the deflection angles of the laser beam, one can create various box (billiard) shapes.

Usually, the studies of atom optic billiards are mainly focused on the dynamics of atom and cooling problem without taking into account the effect of the electronic structure of an atom to the confining force. However, the response of the electronic structure of atom to the shape and geometry of the confinement boundaries plays important role in atom cooling, highly compressed matter and fabrication of nanoscale devices using confined atoms. We note that most of the studies on atom-in-box system available in the literature, deal with the static box walls. However, in many cases, including atom optic billiards [17, 18] and metallic hydrogen formation [7, 8] the boundary of the confinement may fluctuate, or can be time-varying. In this case the dynamics of atomic electron is completely different than that for fixed boundaries.

In this paper we study quantum dynamics of one electron atom confined in a spherical box with time dependent radius by focusing on the response of atomic electron to the effect of moving walls of the box. The time-dependence of the wall's position is considered as non-adiabatic, i.e. we consider the cases of rapidly shrinking, expanding and

breathing boxes.

Study of the problem of moving boundaries in quantum mechanics requires solving the Schrödinger equation with time-dependent boundary conditions. Earlier, the quantum dynamics of a particle confined in a time-dependent box was studied in different contexts (see Ref. [24]-[39]). Here we consider similar problem for an electron moving in a Coulomb field of the atomic nucleus, confined in a spherical box with rapidly varying radius.

This paper is organized as follows. In the next section we give brief description of the atom-in-box problem for a static box. Section 3 presents detailed treatment of the quantum dynamics of the atom confined in a spherical box with moving walls. Analysis of the quantum pressure and force acting on the atom by moving wall of the box is also presented. Finally, section 4 provides some concluding remarks.

II. THE HYDROGEN ATOM IN A STATIC SPHERICAL BOX

Consider hydrogen-like (one-electron) atom confined in a spherical box with impenetrable walls with the radius r_0 . Assuming that the nucleus of the atom is fixed at

the center of box, for the dynamics of atomic electron in such system we have the stationary radial Schrödinger equation which is given as (in atomic, units $m_e = \hbar = e = 1$):

$$\left[-\frac{1}{2} \frac{\partial^2}{\partial r^2} - \frac{1}{r} \frac{\partial}{\partial r} + \frac{l(l+1)}{2r^2} - \frac{Z}{r} \right] R_{nl}(r) = E_{nl} R_{nl}(r), \quad (1)$$

where R_{nl} is the radial part of the wave function, Z is the charge of the nucleus, n and l are the principal and orbital quantum numbers, respectively. The energy eigenvalues, E_{nl} can be found from the boundary conditions for $R_{nl}(r)$ [9, 14]:

$$R_{nl}(r)|_{r=r_0} = 0. \quad (2)$$

In Table 1 first seven energy levels of the confined atom for different box sizes are compared with those of unconfined (free) atom. For the ground state level the eigenvalues of confined and free atoms are the same, while for excited states they become different. For confined atom the levels are slightly higher than those for corresponding free atom energy levels. The difference becomes feasible at highly excited levels and smaller box sizes.

Table 1. The energy spectrum (first few levels) of a hydrogen-like atom confined in a spherical box with the radius r_0 .

n	Confined atom ($r_0 = 70$)	Confined atom ($r_0 = 100$)	Confined atom ($r_0 = 150$)	Free atom
1	-0.5000000	-0.5000000	-0.5000000	-0.5000000
2	-0.1249999	-0.1249999	-0.1249999	-0.1250000
3	-0.0555555	-0.0555555	-0.0555555	-0.0555555
4	-0.0312499	-0.0312499	-0.0312499	-0.0312500
5	-0.0199439	-0.0199999	-0.0199999	-0.0200000
6	-0.0123793	-0.0138684	-0.0138888	-0.0138888
7	-0.0031636	-0.0095963	-0.0102032	-0.0102040

III. HYDROGEN-LIKE ATOM IN TIME-DEPENDENT SPHERICAL BOX

Consider atom confined in a spherical box with time-varying radius given by $r_0 = r_0(t)$. In this case the sphere remains its shape during the expansion(contraction), so that the central symmetry is not broken. Therefore, if atomic nucleus is fixed at the center of sphere, the electron dynamics is described by the time-dependent radial

Schrödinger equation which is given as

$$i \frac{\partial R(r, t)}{\partial t} = H R(r, t), \quad (3)$$

where

$$H = -\frac{1}{2} \frac{\partial^2}{\partial r^2} - \frac{1}{r} \frac{\partial}{\partial r} + \frac{l(l+1)}{2r^2} - \frac{Z}{r}.$$

The boundary conditions for Eq.(3) are imposed as

$$R(r, t)|_{r=r_0(t)} = 0.$$

To solve Eq.(3) one should reduce the boundary conditions into time-independent form. This is can done by using the following transformation [28, 29]:

$$y = \frac{r}{r_0(t)}. \quad (4)$$

In terms of new coordinate, y Eq.(3) can be rewritten as

$$i \frac{\partial R(y, t)}{\partial t} = \left[-\frac{1}{2r_0^2} \frac{\partial^2}{\partial y^2} - \left(\frac{1}{2r_0^2 y} - i \frac{\dot{r}_0}{r_0} y \right) \frac{\partial}{\partial y} + \frac{l(l+1)}{2r_0^2 y^2} - \frac{Z}{r_0 y} \right] R(y, t) \equiv \tilde{H} R(y, t). \quad (5)$$

Using the transformation of the wave function given by

$$R(y, t) = \frac{1}{r_0(t)^{3/2} y} e^{i \frac{1}{2} r_0(t) \dot{r}_0(t) y^2} \Phi(y, t), \quad (6)$$

and introducing of the new time-variable defined as [28, 31, 38]

$$\tau = \int_0^t \frac{ds}{r_0(s)^2},$$

we reduce Eq.(5) into the form

$$i \frac{\partial \Phi}{\partial \tau} = -\frac{1}{2} \frac{\partial^2 \Phi}{\partial y^2} + \left(\frac{1}{2} r_0^3 \ddot{r}_0 y^2 + \frac{l(l+1)}{2y^2} - \frac{Z r_0}{y} \right) \Phi. \quad (7)$$

The boundary condition for Φ is imposed as

$$\Phi(y, t)|_{y=1} = 0.$$

We note that Eq.(7) can be obtained from Eq.(3) by using following unitary transformation [31]:

$$\tilde{H} = e^{-iV} e^{-iU} (H - i \frac{\partial}{\partial t}) e^{iU} e^{iV},$$

where

$$U = -\frac{3}{2} (\hat{r} \hat{p}_r + \hat{p}_r \hat{r}) \ln r_0(t) = i(r \frac{\partial}{\partial r} + \frac{3}{2}) \ln r_0(t),$$

and

$$V = -\frac{1}{2} r_0 \frac{dr_0}{d\tau} y^2.$$

Eq.(7) is the Schrödinger equation for an electron moving in the field of Coulomb and time-dependent harmonic oscillator potentials. The whole system is confined in a spherical box with unit radius. Time and coordinate variables cannot be separated in Eq.(7) and one needs to solve it numerically. To do this we expand $R(y, t)$ in

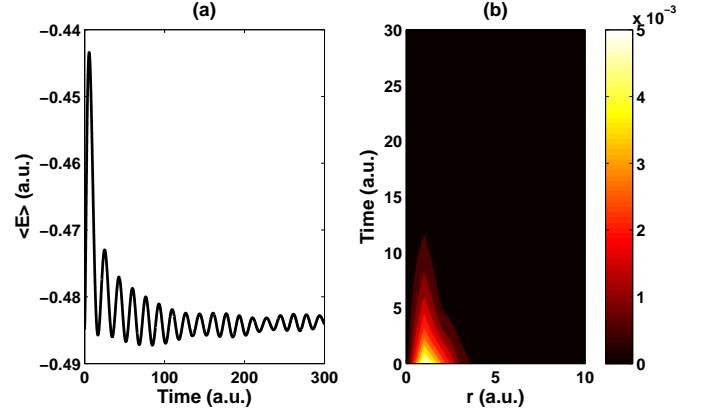


FIG. 1: (Color online) The average binding energy (a) and probability density (b) for hydrogen-like atom confined in a linearly expanding spherical box as a function of time for $a = 10$, $b = 1$.

terms of complete set of eigenfunctions of spherical box with unit radius:

$$\Phi(y, t) = \sum_{nl} C_{nl}(t) \varphi_{nl}(y), \quad (8)$$

where $\varphi_{nl}(y) = N_{nl} j_l(\lambda_{nl} y)$ are the eigenfunctions of the stationary Schrödinger equation for a spherical box of unit radius, j_l are the spherical bessel functions. Inserting this expansion into Eq.(7) we get the system of first order differential equations with respect to $C_{nl}(t)$:

$$i \dot{C}_{nl}(t) = r_0^{-2} \sum_{n'l'} C_{n'l'}(t) V_{nl n'l'}(t) + \varepsilon_{nl} r_0^{-2} C_{nl}, \quad (9)$$

where ε_{nl} are the eigenvalues of the Schrodinger equation for spherical box and

$$V_{nl n'l'}(t) = \langle \varphi_{n'l'} | -\frac{Z r_0}{y} + \frac{1}{2} r_0^3 \ddot{r}_0 y^2 | \varphi_{nl} \rangle.$$

In solving Eqs.(9) numerically one should take into account the normalization condition for the expansion coefficients, C_{nl} :

$$\sum |C_{nl}(t)|^2 = 1,$$

which follows from the normalization condition for the wave function:

$$\int_0^{r_0(t)} |\Psi(r, t)|^2 d^3 r = 1.$$

Having found the wave function, one can compute physical characteristics of the atomic electron, such as average binding energy, force and pressure acting on atom

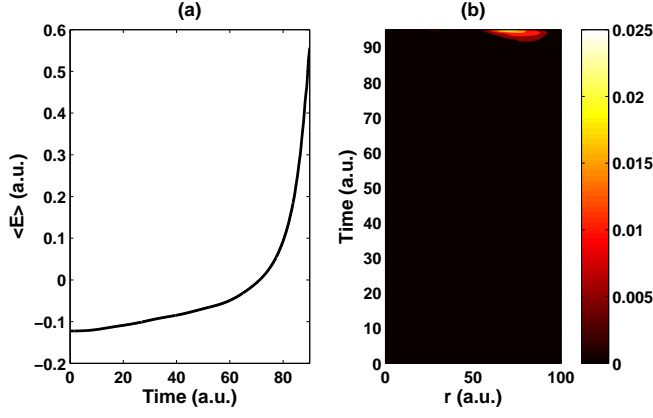


FIG. 2: (Color online) The average binding energy (a) and probability density (b) for hydrogen-like atom confined in a linearly contracting spherical box as a function of time for $a = 100$, $b = -1$.

by considering different regimes of the wall's motion. In the following we will do that for linearly expanding, contracting and harmonically oscillating box wall.

Important physically observable characteristics of the atomic electron is its average binding energy which is defined as

$$\begin{aligned} \langle E(t) \rangle = 4\pi \int_0^{r_0(t)} R^*(r, t) \left(-\frac{1}{2} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) \right. \\ \left. + \frac{l(l+1)}{2r^2} - \frac{Z}{r} \right) R(r, t) r^2 dr. \end{aligned}$$

In Fig. 1 the average binding energy, $\langle E(t) \rangle$ and probability density, $|\Psi(r, t)|^2$ of hydrogen atom confined in a linearly expanding spherical box ($r_0(t) = a + bt$) are plotted as a function of time for $a = 100$, $b = 1$, $Z = 1$. As the initial state (the state of the atom at $t = 0$) we choose the ground state of atom in a static spherical box. The average binding energy decreases in time, as box expands. During long enough time $\langle E(t) \rangle$ asymptotically goes to the value of the ground state energy. This is confirmed by the plot of the probability density $|\Psi(r, t)|^2$, showing that the position of the electron is localized near the center of sphere, as box size grows. This makes atom in such rapidly expanding box very effective tool for de-excitation of atomic electron into the ground state and atom cooling. Indeed, de-excitation of atoms into the ground state is the step needed for their cooling and formation of Bose-Einstein condensation.

Very important case which is attractive from the viewpoint of practical applications, is the contracting box. When box becomes shrink the pressure on the atom cre-

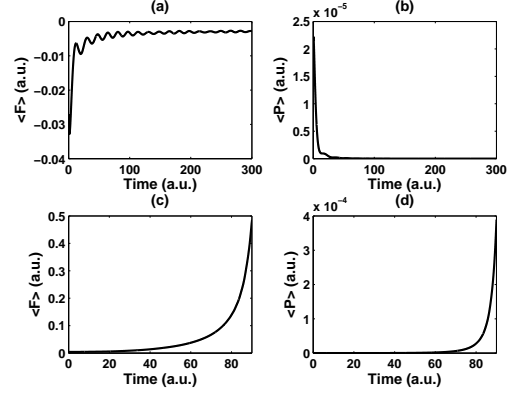


FIG. 3: Time-dependence of the average force (a), (b) and pressure (c), (d) acting on atomic electron by the wall of for linearly expanding ($a = 10, b = 1$) and linearly contracting ($a = 100, b = -1$) spherical boxes.

ated by the wall of shrinking box becomes higher. Such dynamic compression method creating time-dependent pressure is used, e.g. in metallic hydrogen formation experiments [7]. Dynamic high pressure leads to extreme conditions for the atom when the force acting by the wall on the atomic electron becomes higher than that of atomic nucleus.

In Fig. 2 plots of the average binding energy as a function of time and probability density vs time and position of the electron are presented for linearly contracting box ($r_0(t) = a - bt$) for $a = 100$ and $b = 1$. The initial state of atom as fixed as first excited state ($n = 2$) of spherically confined atom. The average binding energy grows almost linearly during initial stage, while upon shrinking into some (critical) box size the growth energy becomes abrupt. Further shrinking leads to becoming the binding energy positive which implies that electron becomes "free" inside the box, i.e. it does not "feel" the Coulomb field of the nucleus under such high pressure. The "critical" size of the box at which "ionization" and sudden growth of the average binding energy occur corresponds to $r_0(t) \approx 25$. Thus under such extremely high pressure created by shrinking box, atomic electron becomes free with respect to nucleus and it will become "electron-in-box" system. Electron is localized near the moving wall during the whole expansion time.

An important characteristics which are responsible for the behavior of atomic electron in time-dependent box are the average force acting on the atomic electron by the moving wall and pressure on the atom created by the wall.

The force operator for time-dependent box is given by [38, 39]

$$\hat{F} = -\frac{\partial \hat{H}}{\partial r_0(t)}. \quad (10)$$

The average force can be calculated as [38]

$$\langle F(t) \rangle = -\frac{\partial}{\partial r_0(t)} \langle R(r, t) | \partial \hat{H} | R(r, t) \rangle. \quad (11)$$

where $R(r, t)$ is the wave function of the atomic electron in time-dependent box determined by Eq.(3).

Then the average pressure on the atom created by the moving wall can be written as

$$\langle P(t) \rangle = \frac{\langle F(t) \rangle}{4\pi r_0^2(t)}.$$

Fig. 3 presents plots of the average force acting on the atomic electron by the box wall and the average pressure on atom created by box as functions of time for linearly expanding and contracting boxes. The values of the parameters are the same as those in Figs. 1 and 2. For linearly expanding box the modulus of the force acting on the electron by moving wall decays on time, asymptotically approaching zero. The value of the pressure for this system also decreases in time approaching zero in long time limit. For linearly contracting box (Fig. 3b) the behaviors of the average force and pressure are completely different than those for expanding one. Sudden growth of the average force and pressure starts from some critical size of the box, $r_0(t) = 25$. This is very high pressure (few GPa) which can be achieved dynamical compression method used, e.g. in metallic hydrogen formation [7, 8]. From the viewpoint of metallic hydrogen physics, such pressure can cause appearing of "free electron gas" before the formation of metallic hydrogen.

Finally, consider the case of harmonically oscillating walls given by $r_0(t) = a + b \cos \omega t$, where ω and b are the oscillating frequency and amplitude, respectively. In Fig. 4 the average binding energy and probability density are plotted for $\omega = 1$, $b = 10$ and $a = 100$. The average binding energy grows during some initial period after that suppression of the growth can be observed and $\langle E(t) \rangle$ does not cross the boundary of the continuum. In other words, no ionization is possible for this value of the oscillation amplitude, b . Similar "saturation" can be observed in the time-dependence of the average force and pressure acting on atomic electron by moving wall. However, for higher oscillation amplitudes interaction of atomic electron with the breathing wall leads to ionization of atom during some (finite) time interval. Indeed,

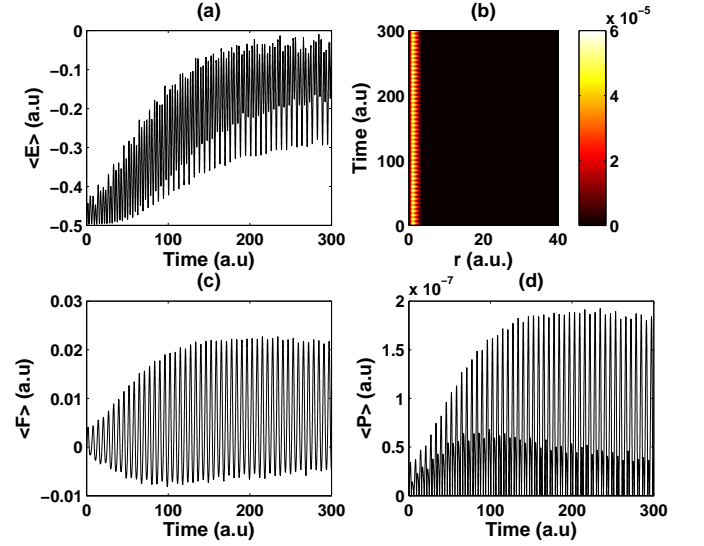


FIG. 4: (Color online) Time-dependence of the binding energy (a), probability density (b), average force (c) and pressure (d) acting on atomic electron by the wall for harmonically breathing box ($a = 100, b = 10, \omega = 1$) spherical box.

as shows the plot of $\langle E(t) \rangle$ in Fig. 5, the average binding energy grows and crosses the border of the continuum. The growth of the energy is continued after the ionization. Similar growth exhibit the average force and pressure as a functions of time. Thus there is a "critical" value (approximately 12a.u. in our case) of the breathing amplitude at which ionization will occur. No ionization is possible at the values below this critical amplitude, although diffusive excitation occurs. It is clear that oscillation of the box's wall leads to pumping of the energy to atom which causes excitation and ionization of atom during long enough time. In other words, atom in a box with oscillating walls is to some extent equivalent to that in a monochromatic field widely studied earlier in the context of chaotic ionization [40–42]. However, unlike the usual diffusive ionization which occurs in highly excited atom, in the above model diffusion of the atomic electron through the energy levels may start at lower lying states, too. Such model can be realized in atom optics billiard where oscillating billiard boundaries can be created by tightly focused laser beam with time-varying position [17–20].

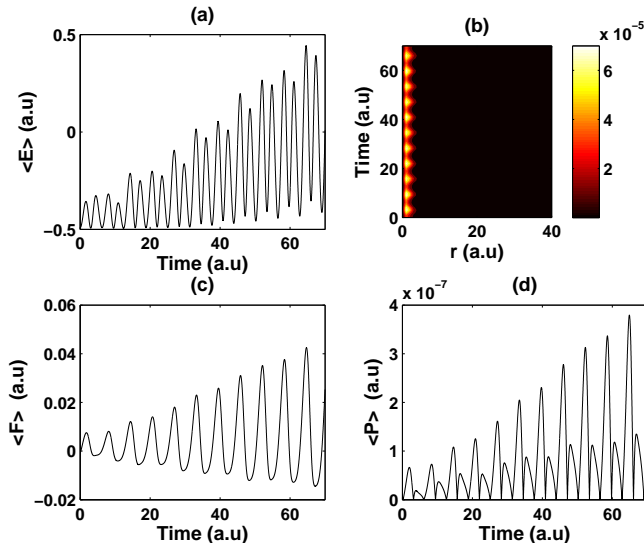


FIG. 5: (Color online) Time-dependence of the binding energy (a), probability density (b), average force (c) and pressure (d) acting on atomic electron by the wall for harmonically breathing box ($a = 100, b = 15, \omega = 1$) spherical box.

IV. CONCLUSIONS

In this work we studied quantum dynamics of a hydrogen-like atom confined in a impenetrable spherical

box with time-dependent radius by considering rapidly expanding, contracting and oscillating (breathing) walls. The main focus of the study is given to the response of the atomic electron's dynamics to the moving wall of the box.

Time-dependence of the binding energy of the electron, probability density, average force and pressure are analyzed for linearly expanding, contracting and harmonically oscillating walls. For rapidly expanding box de-excitation of the atomic electron leading to decreasing of average binding energy occurs. Rapidly contracting box causes creation of higher pressure on atom and ionization of atomic electron. i.e. atomic electron becomes unbound in the field of nucleus, although confined inside the box. In case of harmonically breathing sphere, atom behaves itself as that in microwave electric field where the diffusive (multi-step) excitation and ionization of atom will occur.

The above models can be used in practically important problems, such as metallic hydrogen formation, atom cooling and modeling the behavior of matter under extreme conditions caused by high pressures. In addition, atom-in-spherical box with varying radius can be effective model to describe quantum dynamics in atom optics billiards.

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- [1] C. Gardiner, P. Zoeller, *The Quantum World of Ultra-Cold Atoms and Light Book II: The Physics of Quantum-Optical Devices*, World Scientific (2015).
 - [2] T. Tsurumi, H. Hirayama, M. Vacha, T. Taniyama, *Nanoscale Physics for Materials Science*, CRC Press (2009).
 - [3] P. Meystre, *Atom Optics*, Springer (2001).
 - [4] *Theory of Confined Quantum Systems-Part One*, J.Sabin and E. Brandas (Eds.), Advances in Quantum Chemistry Academic, **57** (2009).
 - [5] K.D. Sen (Eds), *Electronic Structure of Quantum Confined Atoms and Molecules*. Springer (2014).
 - [6] V.D. Blank, E.I. Estrin, *Phase Transitions in Solids Under High Pressure*, CRC Press (2013)
 - [7] J.M. McMahon, M.A. Morales, C. Pierleoni, D.M. Ceperley, *Rev.Mod.Phys.*, **84** 1607 (2012).
 - [8] Ji Chen, Xin-Zheng Li, Qianfang Zhang *et.al.*, *Nature Commun.* **4**, 2064 (2013).
 - [9] A. Michels, J. de Boer, and A. Bijl, *Physica (The Hague)* **4** 981 (1937).
 - [10] A. Sommerfeld and H. Welker, *Ann. Phys.* **32** 56 (1938).
 - [11] I. Last and Th. F. George, *Chem. Phys. Lett.* **142** 19 (1987).
 - [12] Sh. Kang, Y-Ch. Yang, J. He, F-Q. Xiong, N. Xu, *Cent. Eur. J. Phys.* **11** 584 (2013).
 - [13] Sh-G. Zhou, J. and E-G. Zhao, *J. Phys. B: At. Mol. Opt. Phys.* **42** 245001 (2009).
 - [14] D. R. Maovic, *Cent. Eur. J. Phys.* **10** 768 (2012).
 - [15] E. Ley-Koo and S. Rubinstein, *J. Chern. Phys.* **71** 351 (1979).
 - [16] M. Capitelli, *Phys. Rev. A* **80** 032113 (2009).
 - [17] V. Milner, J. L. Hanssen, W. C. Campbell, and M. G. Raizen, *Phys.Rev.Lett.* **86** 8 (2001).
 - [18] A. Kaplan, N. Friedman, M. Andersen, and N. Davidson, *Phys.Rev.Lett.* **87** 27 (2001).
 - [19] M. F. Andersen, A. Kaplan, N. Friedman and N. Davidson, *J. Phys. B: At. Mol. Opt. Phys.* **35** 2183 (2002).
 - [20] B. Rohwedder, *EPL* **60** 505 (2002).
 - [21] S. Montangero, D.Frustaglia, T.Calarco and R. Fazio, *EPL* **88** 30006 (2009).
 - [22] N. Friedman, A. Kaplan, *Adv. At. Mol. Phys.* (2002).
 - [23] A. D. Stone, *Nature* **465** 10 (2010).
 - [24] S. W. Doescher and H. H. Rice, *Am. J. Phys.* **37** 1246 (1969).

- [25] A. Munier, J. R. Burgan, M. Feix and E. Fijalkow, J. Math. Phys. **22** 1219 (1981).
- [26] D. N. Pinder, Am. J. Phys. **58** 54 (1990).
- [27] P. Pereshogin, P. Pronin, Phys. Lett. A **156** 12 (1991).
- [28] A. J. Makowski and S. T. Dembinski, Phys. Lett. A **154** 217 (1991).
- [29] A. J. Makowski and P. Peptowski, Phys. Lett. A **163** 142 (1992).
- [30] A. J. Makowski, J. Phys. A: Math. Gen. **25** 3419 (1992).
- [31] M. Razavy, Phys. Rev. A **44** 2384 (1991).
- [32] D. A. Morales, Z. Parra, R. Almeida, Phys. Lett. A **185** 273 (1994).
- [33] C. Yuce, Phys. Lett. A **321** 291 (2004).
- [34] P. Seba. Phys. Rev. A **41** 2306 (1990).
- [35] C. Scheiniger and M. Kleber, Physica D **50** 391 (1991).
- [36] J.D. Lejarreta, J. Phys. A. **32**, 4749 (1999).
- [37] T. K. Jana, P. Roy, Phys. Lett. A. **372**, 2368 (2008).
- [38] K Nakamura, Z.S. Sobirov, D Matrasulov, S.K.Avazbaev and T.Monnai, Phys. Rev. E **83**, 041133 (2011).
- [39] K Nakamura, Z.S. Sobirov, D Matrasulov, S.K.Avazbaev, Phys. Rev. A **86**, 061128 (2012).
- [40] G. Casati, B. V. Chirikov, and D. L. Shepelyansky, Phys. Rep. **154**, 77 (1987).
- [41] R. V. Jensen, S. M. Susskind, and M. M. Sanders, Phys. Rep. **201**, 1 (1991).
- [42] P.M. Koch, K.A.H. van Leeuwen, Phys. Rep. **255**, 289 (1995).